Biofuels production in conventional oil refineries through bio-oil co-processing

Joint workshop of ENMIX, FASTCARD, CASCATBEL, BIOGO

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Date: 21 January, 2016
TOPICS

- European regulation
- Bio-challenge. Available technologies
- Bio-challenge. Utilize existing refinery infrastructure
- FASTCARD project
European regulation
Preparing the transition to advanced biofuels

2020 climate & energy package

FQD: 6% cut in GHG emissions

RED: 20% of EU energy from renewables

20% improvement in energy efficiency
European regulation
Preparing the transition to advanced biofuels

Renewable Energy Directive

10% bioenergy target for all transport fuels by 2020

7% cap on use of 1st generation biofuels

3% cap on use of 2nd generation feedstocks

Double counting of feedstocks for advanced biofuels

0.5% advanced biofuels (reference value)

Reporting on GHG emission savings
European regulation
Preparing the transition to advanced biofuels

(3) The following Annex is added:

"ANNEX IX

Part A. Feedstocks and fuels, the contribution of which towards the target[...] referred to in the first subparagraph of Article 3 [...] (4) shall be considered to be twice their energy content

(a) Algae if cultivated on land in ponds or photobioreactors.
(b) Biomass fraction of mixed municipal waste, but not separated household waste subject to recycling targets under point (a) of Article 11(2) of Directive 2008/98/EC.
(c) Bio-waste as defined in Article 3(4) of Directive 2008/98/EC from private households subject to separate collection as defined in Article 3(11) of that Directive.
(d) Biomass fraction of industrial waste not fit for use in the food or feed chain, including material from retail and wholesale and the agro-food and fish and aquaculture industry, and excluding feedstocks listed in part B of this Annex.
(e) Straw.
(f) Animal manure and sewage sludge.
(g) Palm oil mill effluent and empty palm fruit bunches.
(h) Tall oil pitch."
BIO-Challenge!! Available technologies

EU Transport Fuels
Bioenergy Requirement 2020

Minimum 3% bioenergy from 2\textsuperscript{nd} generation feedstocks:
- Waste oils based Green Diesel
- RTP green fuel FCC co-processing
- Cellulosic Ethanol

Maximum 7% bioenergy from 1\textsuperscript{st} generation feedstocks:
- Vegetable Oil based Green Diesel
- Sugar/starch based Ethanol / ETBE
- Vegetable Oil based FAME

SOURCE: UOP
**BIO-Challenge!! Utilize existing refinery infrastructure**

- **Utilize existing refinery**
- **Cost effective**
- **High demand of biofuels**

- **ETBE**
- **FAME**
- **HVO**
- **Bio-oil to FCC**
HVO market in Europe

H2
Biological feedstock
HDT
HVO
Propane

SOURCE: GREENEA
Bio-oil FCC co-processing

Biomass → PYROLYSIS PROCESS → Bio-oil

FCC UNIT

LPG → Gasoline → LCO → DO

Partially renewable products to fuels blending
Bio-oil FCC co-processing
Bio-oil FCC co-processing

Heat Generated by Coke Combustion:

\[
\begin{align*}
C + \frac{1}{2}O_2 & \rightarrow CO \\
CO + \frac{1}{2}O_2 & \rightarrow CO_2 \\
2H + \frac{1}{2}O_2 & \rightarrow H_2O
\end{align*}
\]

Riser exit temperature controlled by Catalyst Circulation Rate which is controlled by the Rg. Cat. Slide Valve opening (control loop)

Regenerator Flue Gas

Stripping Steam

Feed injection

220°C

Regenerator Air

720°C

530°C

525°C

735°C
Bio-oil FCC co-processing
Reactions in FCC process

Crackability (Conversion): Paraffinic > Naphthenic > Aromatic
Coke-forming tendency (Heat Balance): Paraffinic < Naphthenic < Aromatic
Bio-oil FCC co-processing
Reactions in FCC process
Why co-FCC?

Key results: Unit Throughputs

- Throughput of gasoline-producing FCC units drops dramatically, due to declining gasoline demand.
- Significant capacity additions required in diesel-producing units (Hydrocracking), Residue conversion units (Coking) and Hydrogen production units.
  - Driven by IMO bunker sulphur reduction and growing demand share of distillates.
  - Requires massive investment in new unit capacity.

No H2 consumption

Oil company
Two catalyst-based pathways for conversion of biomass to advanced biofuels with 4 catalytic processes:

- Pyrolysis **LIQUID route** (short term): hydrotreating of pyrolysis oil + co-processing in FCC
- Gasification **GAS route** (long term): Hydrocarbon reforming + Fischer Tropsch synthesis
FASTCARD project. Liquid line

Liquid baseline (carbon balance: %C from biomass to products):

- Pyrolysis
- Stabilisation
- Deoxygenation
- Refined Oil (RO) to FCC

PL
- C = 100%
- C = 65%
- C = 65%

SPO
- C > 60%
- Gas: C < 2%
- H2
- Water: C < 2%
- Water: C < 4%

RO
- Gas: C < 16%
- C > 40%
- wt.%
- C_{daf} 89.0
- H_{daf} 11.0
- O_{daf} -
- H_{2}O -
**FASTCARD project. Liquid line Integration between HDO / FCC**

- **Carbon efficiency**
- **+ H₂ consumption. + OPEX / CAPEX**
- **+ E intensity (CO₂)**
- **Improves bio-oil quality**

**Impact on HDO**
- **Increase severity in HDO**

**Impact on FCC**
- **Improves processability**
- **Better selectivity**
- **- catalysts deactivation**
- **+ cost of feedstock**

**Balance??**
FASTCARD concept. Liquid line
Co-FCC challenges

- Identify new catalysts (new materials) to have high cracking of bio-oil and overcome coke production from bio-oil.
- To scale de results from MAT unit (fix bed) to pilot plant (fluidized catalyst).
- Optimize bio-oil injection in pilot plant ¿Best feed point injection?

Lab scale: MAT
Pilot plant
FASTCARD concept. Liquid line
Limitations and challenges

• Pyrolysis oil properties: worse than fossil feedstock
  ✓ High oxygenated / water content = unstable, reactive, acid (corrosion), polar product

• HDO limitations
  ✓ Conventional HDT catalysts (CoMoS, NiMoS / Al2O3) deactivate rapidly and Al2O3 promotes undesirable reactions. Require sulphidation (S)
  ✓ Extensive research in new catalyst for bio-oil HDO, most noble metal-based (expensive)
  ✓ HDO is energy intensive: high H2 consumption (> 400 Nl/kg), high pressure
  ✓ Low carbon efficiency < 60% and high methane formation (>5%)

• Co-FCC limitations
  ✓ Undesirable selectivity (lower liquid / higher gas and coke) with conventional FCC catalyst
  ✓ Higher catalyst deactivation. Could be improved with higher rare earth, but it increase the cost
  ✓ Objective: develop new catalyst for co-FCC with bio-oil
FASTCARD concept. Liquid line
Objectives and achievements

- Develop a **Downscaling/Upscaling approach** to decrease development time
  - State of Art baseline established (real feed, SoA catalysts)
  - Downscaling and alignment between industrial plant, pilot plant and laboratory completed successfully

- Develop powerful **modeling tools** adapted to bio-feedstock
  - Comprehensive dataset from WP3 and 4 provided to WP5 / WP6 as base for modelling and economic calculations
  - Modelling development progressing
FASTCARD concept. Liquid line
Objectives and achievements

- Develop **new nano-catalysts** for the catalytic processes addressed by the project:
  - Impact of co-feeding different qualities of bio-oil under study
    - PL, SPO, 8 PDO and RO tested at lab scale in MAT (CNRS and Grace)
    - RO and PDO successfully co-processed at pilot scale
  - 17 zeolite materials synthetized and hydrothermal stability evaluated
  - Several materials show equal or higher stability compared to USY
  - MCM-22 shows very promising hydrothermal stability and acidity retention during deactivation
  - Zeolite Beta showed better long term conversion with n-decane than USY